Chapter 17 (11th edition) or 18 (10th and previous editions) Entropy, Free Energy and Equilibrium

Entropy, Free Energy, and Equilibrium unit has had its Chapter changed to 17 in the 11th edition. It's just a move in position. The condensed digital version I is the 10th edition, so I will keep the Chapter 18 designation.

There are significant parts of the sections that you can skip. Use the summary to focus on what is required for AP Chemistry.

> "Die Energie der Welt ist constant
> Die Entropie der Welt strebt einem Maximum zu."
> Rudolf Julius Emanuel Clausius, *Mechanische Warmetheorie*, 1879

Chemistry by Chang and Goldsby 18.01 The Three Laws of Thermodynamics 18.02 Spontaneous Processes 18.03 Entropy 18.04 The Second Law of Thermodynamics 18.05 Gibbs Free Energy 18.06 Free Energy and Chemical Equilibrium 18.07 Thermodynamics of Living Systems	I have posted a condensed version of Chang's 10th edition Chapter 18 on the classroom webpage that you can use with this summary.

18.1 The laws of thermodynamics: Energy is conserved, and Entropy increases.

That's all you need to know in this unit.

18.2 Spontaneous Processes

For AP Chemistry, spontaneous processes are called **Thermodynamically Favored Processes**.
Most chemistry courses, texts, and chemists prefer the shorter term, "spontaneous processes".

Thermodynamically favored processes may proceed → to favor the products.

However, if the reaction has a high activation energy, the reaction may take forever to make those products.

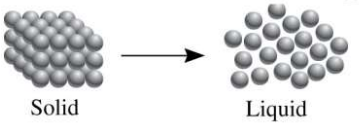
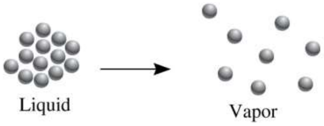
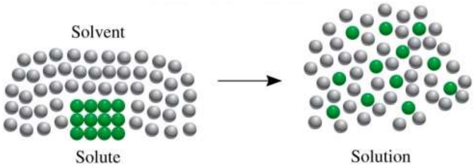
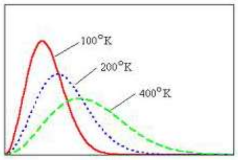
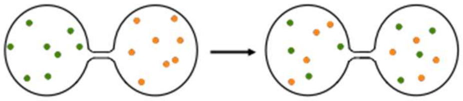
AP15 Thermodynamics determines if the reaction will go forward, be at equilibrium, or reverse.

AP12 Kinetics (reaction rates) controls how quickly a reaction progresses.

18.3 Entropy, S, is a measure of dispersal of matter or energy. Entropy is one of the two factors that determine K_{eq}

It is common to say that entropy is the measure of "disorder" of a system. While the term "disorder" is easy to understand, the terminology to use in AP Chemistry is "Entropy increases when matter or energy becomes more dispersed." When explaining a change in entropy, be sure to include descriptions of atoms or molecules. If the atoms or molecules become more "dispersed" or become freer to move, then entropy is increased.
Skip microstate probability, W. Microstates and W are not part of the AP curriculum.

Know the increases in entropies of the six types of changes as shown in the table below.

Changes that **Increase Entropy, ΔS = +**	
Solid → liquid  	Liquid → gas or any increase in volume 
Solute and solvent mix to make a solution.  …with notable exceptions[1]	Increase in Temperature (avg KE)  Energy is more dispersed as temperature increases.
Increase in number of moles of particles. $A \rightarrow B + C$ Δn = positive	Mixing of particles, and atoms forming molecules  and $A_2 + B_2 \rightarrow AB + AB$

18.4 The Second Law of Thermodynamics

The Entropy of the universe is increasing. This contrasts with the Conservation of Energy where the energy of the universe is constant. Locally a system's entropy can be decreased, but only because the effort required to decrease entropy locally leads to an increase in entropy of the surroundings which more than compensates for the local decrease.

The symbol for entropy is ***S* and the unit for entropy is J/mol K.**

Comparing the entropy of products to reactants: $\Delta S_{rxn}^\circ = \Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}}$

---

[1] There can be a decrease in entropy if the randomly arranged water molecules become more orderly by clustering in a regular manner around the solute particles. This occurs often with around small highly charged ions such as Al^{3+}.

Entropy is used in conjunction with enthalpy, so a comparison of enthalpy and entropy is in order.

<table>
<tr><td>S , Entropy – a measure of “dispersion of matter”.</td><td>H , Enthalpy – the internal energy of a substance</td></tr>
<tr><td>S values measurable and are all positive.
The lowest S, 0 J/K, is that of a crystalline substance at absolute zero.
$S°$ of a substance is a positive number[2].
$\Delta S_{rxn}°$ can be positive or negative.</td><td>H cannot be determined. Only comparative enthalpies, ΔH, can be measured from the change in heat energy or work in a reaction.
$H°$ is impossible to measure.
$\Delta H_{rxn}°$ can be positive or negative.</td></tr>
<tr><td>S and ΔS are measured in J/mol K.
S and ΔS are usually less than 1000 J/mol K.</td><td>ΔH is measured in kJ/mol
ΔH is usually more than 1000 J/mol.</td></tr>
<tr><td>S values don’t always require Δ.
Entropy tables list the absolute entropies of substances. It is possible to determine the total amount of entropy of a substance.
No substance can have an entropy of less than zero.</td><td>H values always require a Δ.
Enthalpy values are always based on a change that occurs in a reaction.
ΔH_f, the change in enthalpy that occurs as a substance is made from its elements.
By definition, elements have a ΔH_f of 0 kJ/mol. Thermo tables on the exam will not give the ΔH_f values for elements since students are expected to know this.</td></tr>
<tr><td>Sample values from an entropy table:
<table>
<tr><th>Substance</th><th>$S°$ (J/mol K)</th></tr>
<tr><td>$Al(s)$</td><td>28</td></tr>
<tr><td>$Al(g)$</td><td>164</td></tr>
<tr><td>$AlCl_3(s)$</td><td>111</td></tr>
</table></td><td>Sample values from an enthalpy table:
<table>
<tr><th>Substance</th><th>$\Delta H_f°$ (kJ/mol)</th></tr>
<tr><td>$Al(s)$</td><td>see box above</td></tr>
<tr><td>$Al(g)$</td><td>326</td></tr>
<tr><td>$AlCl_3(s)$</td><td>-704.2</td></tr>
</table></td></tr>
<tr><td colspan="2">IMPORTANT!
When working with equations involving both entropy and enthalpy, change the <i>S</i> values to kJ/mol K so that both $\Delta H°$ and $S°$ are in kJ.</td></tr>
<tr><td>$\Delta S_{rxn}° = +$, are thermodynamically favored.
Reactions are where the products have more entropy than the reactants, $\Delta S = +$, are favored.</td><td>$\Delta H_{rxn}° = -$, are thermodynamically favored.
Exothermic reactions are where the products have stronger bonds than reactants, $\Delta H =$, are favored.</td></tr>
<tr><td colspan="2">There may be a conflict between $\Delta S_{rxn}°$ and $\Delta H_{rxn}°$ where one change is thermodynamically favored, and the other is not. When this occurs, the kJ values of both are compared to determine if the reaction may occur at a given temperature. More on this later.</td></tr>
</table>

---

[2] There are some negative values, but these are unusual aqueous ion instances that you will not need to worry about.

Entropy Changes in the Surroundings

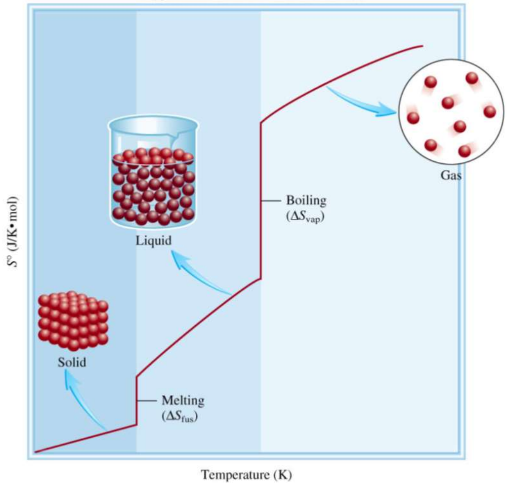
Skip this section.

The Third Law of Thermodynamics and Absolute Entropy

A perfect crystal at absolute zero has zero entropy, $S = 0$.

Look carefully at Figure 18.5. Entropy gradually increases with temperature and has dramatic increases with phase changes such as fusion (melting) and especially vaporization.

When explaining changes in entropy in FRQs, always refer to the atoms' conditions as part of your explanation. e.g., "When liquids change to gases, the atoms are more dispersed and thus entropy is increased."



18.5 And 18.6 Gibbs free energy, is the Bottom Line of a Reaction!

The "net movement" of a reaction is measured by **ΔG, Free Energy**

The predictive statements of ΔG refer to standard conditions where solutions (both reactants and products) start at 1 *M,* and gases (reactants and products) start at 1 atm.
Starting with equal reactants and products makes the evaluation of the direction of the reaction "fair".

Since both products and reactants start off at 1, the reaction quotient, Q (products over reactants) = 1.
Based on starting with **$Q = 1$,** there are **three possible free energy situations.**

First free energy situation:

$\Delta G°$ = negative value Thermodynamically favored $A \rightarrow B$

A negative ΔG^o equilibrium means that the K_{eq} is large (greater than 1) . With $Q < K_{eq}$ the products are favored.

A $\Delta G°$ negative reaction can be harnessed to do work as it moves forward from standard conditions.

If $\Delta G°$ is -25 kJ/mol or even more negative (rule of -25), the reaction goes to completion.

You won't have to bother with an equilibrium expression.

The reaction will just be a simple stoichiometry RICE → problem.

If the reaction is also kinetically favored (high reaction rate, k), the reaction will quickly make the thermodynamically favored products.

If the reaction is not kinetically favored (small reaction rate, k), the reaction may take a very, very long time to make the thermodynamically favored products.

Second free energy situation:

$\Delta G° = 0$ thermodynamically neutral $A \rightleftarrows B$

All the substances starting off at standard conditions, 1 atm and 1 *M*, stay that way, **K_{eq}, = 1**.

Third free energy situation:

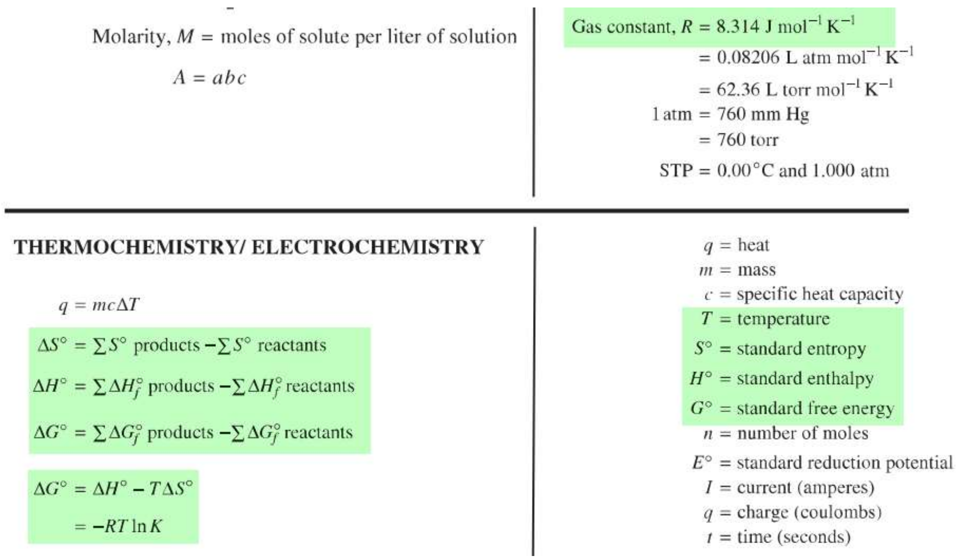
$\Delta G°$ = positive Reverse reaction favored A ← B

When $\Delta G°$ for a reaction is positive, the reaction is thermodynamically favored starting with standard conditions to go in the **reverse direction.**

Products will decrease from their standard 1 *M* and 1 atm concentration, and the reactants will increase to greater than 1 *M* and 1 atm concentrations.

For positive $\Delta G°$ reactions, A← B predominates when both products and reactants start at 1 *M* or 1 atm.

The only way this reaction can move forward is for it to be forced either by a coupled reaction that is thermodynamically favored or if some other source of energy is introduced e.g electrolysis or light photons as in photosynthesis.



Molarity, M = moles of solute per liter of solution

$A = abc$

Gas constant, $R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$

$= 0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1}$

$= 62.36\ \text{L torr mol}^{-1}\ \text{K}^{-1}$

1 atm = 760 mm Hg

= 760 torr

STP = 0.00°C and 1.000 atm

THERMOCHEMISTRY/ ELECTROCHEMISTRY

$q = mc\Delta T$

$\Delta S° = \sum S°$ products $- \sum S°$ reactants

$\Delta H° = \sum \Delta H_f°$ products $- \sum \Delta H_f°$ reactants

$\Delta G° = \sum \Delta G_f°$ products $- \sum \Delta G_f°$ reactants

$\Delta G° = \Delta H° - T\Delta S°$

$= -RT \ln K$

q = heat

m = mass

c = specific heat capacity

T = temperature

$S°$ = standard entropy

$H°$ = standard enthalpy

$G°$ = standard free energy

n = number of moles

$E°$ = standard reduction potential

I = current (amperes)

q = charge (coulombs)

t = time (seconds)

The Gibbs free energy is linked to the equilibrium constant.

$\Delta G° = -RT \ln K$ The antilog of this equation is not on the equation sheet. $K_{eq} = e^{-\frac{\Delta G°}{RT}}$

R, the energy version of the gas constant, is 8.31 J $\text{K}^{-1}\text{mol}^{-1}$

R uses J and the $\Delta G°$ will be in J/mol_{rxn} that should then be changed to kJ/mol_{rxn}.

T, Standard temperature for thermodynamics is 298 K

At standard conditions, the thermal energy factor, *RT*, is an easily remembered number.

RT = (8.31 J/K mol × 298 K) = 2,450 J/mol = **2.45 kJ/mol.**

Bottom Line: Use the rounded thermal energy factor of **2.5 kJ/mol** for *RT* to quickly estimate the equilibrium constant from the standard Gibbs free energy at room temperature.

$$\Delta G° = -(2.5\ \text{kJ/mol}) \times \ln K \qquad K_{eq} = e^{-\frac{\Delta G°}{2.5\ \text{kJ/mol}}}$$

Gibbs free energy	*Equilibrium expression constant value*	**Shift from standard conditions** reactants and products initially 1 atm or 1 *M*. $Q_{initial} = 1$	Estimate of magnitude of *K* *Rule of 25 kJ* $K_{eq} = e^{-\frac{\Delta G^\circ}{2.5\ \text{kJ/mol}}}$
If $\Delta G^\circ > 0$ then…	$0 < K_{eq} < 1$ K_{eq} is small	From standard conditions $Q_{initial} = 1$ $Q > K \quad \underset{\longleftarrow}{\rightarrow}$ $\frac{\text{[products will decrease]}}{\text{[reactants will increase]}}$ Reaction ← and decreases *Q* until Q_{final} = the low value of K_{eq}	$K_{eq} = e^{-\frac{25\ \text{kJ/mol}}{2.5\ \text{kJ/mol}}}$ $K_{eq} = e^{-10} \approx 10^{-5}$ If ΔG° is +25 kJ or larger positive value, K_{eq} will be so small that the resulting equilibrium mixture will have almost **no products at equilibrium.** You will have mostly reactants.
If $\Delta G^\circ = 0$ then …	$K_{eq} = 1$	Concentrations or pressures of reactants and products are at 1 atm or 1 *M* at equilibrium	$K_{eq} = e^{-\frac{0}{2.5\ \text{kJ/mol}}}$ $K_{eq} = e^{0} = 1$
If $\Delta G^\circ < 0$ then…	$1 < K_{eq}$ K_{eq} is large	From standard conditions $Q_{initial} = 1$ $Q < K \quad \overset{\longrightarrow}{\leftarrow}$ $\frac{\text{[products will increase]}}{\text{[reactants will decrease]}}$ Reaction → and increases *Q* until Q_{final} = the large value of K_{eq}	$K_{eq} = e^{-\frac{-25\ \text{kJ/mol}}{2.5\ \text{kJ/mol}}}$ $K_{eq} = e^{10} \approx 10^{5}$ If ΔG° is -25 kJ or a larger negative value, K_{eq} will be so large that the resulting equilibrium mixtures have almost no reactants left at equilibrium. **Reaction proceeds stoichiometrically to completion**.

With more than +25 kJ/mol or –25 kJ/mol for ΔG°, you get extreme values for the equilibrium!

When ΔG° kJ/mol values are single digits, the equilibrium mixes have reactants and products in significant amounts and will require an ICE table and an equilibrium expression.

Bottom line: The more negative the Gibbs free energy is, the larger the equilibrium constant.

Gibbs free energy is determined by the changes in enthalpy and temperature × entropy.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The Driving Forces within Gibbs free energy

(1) Enthalpy changes	**Decreases in enthalpy** (negative Δ*H*) are caused by drops in potential energy because of the formation of stronger bonds. Decreases in enthalpy will drive a rxn →
(2) Entropy changes × Temperature	**Increases in entropy** (positive Δ*S*) will lead to greater dispersion of matter or energy. Increases in entropy will drive a rxn →. The **entropy effect is magnified by increased temperature**.

Important! When doing Gibbs free energy calculations, **change Δ*S*° units** from J/K to kJ/K to match the kJ of Δ*H*.

Know the thermodynamic consequences of each these enthalpy-entropy sign combinations.

In the eaction A ⇄ B with both reactants and products initially at 1 *M* or 1 atm.

When the sign of enthalpy and entropy are the opposite, there is only one Gibbs free energy outcome.

ΔH°	ΔS°	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$	**Reaction A ⇄ B**	***K***
(-) →	(+) →	**Δ*G*° = always (-)** Δ*G*° = (→) and (T→)	Both Δ*H*° and Δ*S*° favor the → rxn. The forward rxn is thermodynamically favored for all temperatures.	K > 1
(+) ←	(-) ←	**Δ*G*° = always (+)** Δ*G*° = (←) and (T←)	Both Δ*H*° and Δ*S*° favor the ← rxn . The reverse rxn is thermodynamically favored for all temperatures.	$0 < K < 1$

When the signs of Δ*H*° and Δ*S*° are the same, the temperature determines the direction of the reaction.

ΔH°	ΔS°	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$	**Δ*H*° and T × Δ*S*° Conflict**	***K***
(-) →	(-) ←	**Δ*G*° = (?)** Δ*G*° = (→) and (T←)	Δ*H*° favors the → rxn. Δ*S*° favors the ← rxn. Increases in temperature magnify the entropy factor and will decrease *K*.	$K = e^{-\frac{\Delta G^\circ}{RT}}$
(+) ←	(+) →	**Δ*G*° = (?)** Δ*G*° = (←) and (T→)	Δ*H*° favors the ← rxn. Δ*S*° favors the → rxn. Increases in temperature magnify the entropy factor and will increase *K*.	

Melting and boiling phase changes are endothermic and involve increases in entropy, so the melting and boiling are dependent on temperature.

Melting and boiling temperatures are equilibrium conditions because both phases co-exist at these temperatures.

At melting and boiling temperatures, the Gibbs Free Energy Equation equals zero.

Therefore, at melting and boiling points $\Delta H°_{\text{phase change}} = T_{phase\ change} \times \Delta S°$

The change in enthalpy is easy to find using calorimetry, and the phase change temperature is easy to find too. Enthalpy of fusion or vaporization can be used to experimentally find the change in entropy of a reaction.

At any equilibrium $\Delta H° = T\Delta S°$

Coupled reactions

Some reactions which are not thermodynamically favored, $\Delta G° = +$, can be manipulated to occur “spontaneously” by harnessing another thermodynamically favored reaction.

Coupling of two reactions:

The first reaction has a positive ΔG and low K_{eq} which is not thermodynamically favored and is driven by a second negative ΔG with a large K_{eq} reaction.

Turning metal sulfides into pure metal is not thermodynamically favored. However, the combustion of sulfur is spontaneous and can be coupled with the metal sulfide reaction to produce a thermodynamically favored reaction.

Rxn 1: $ZnS \rightarrow Zn + S$	$\Delta G° = +198.$ kJ/mol	not thermodynamically favored (rule of +25)
Rxn 2: $S + O_2 \rightarrow SO_2$	$\Delta G° = -300.$ kJ/mol	thermodynamically favored (rule of -25)
Net Rxn: $ZnS + O_2 \rightarrow Zn + SO_2$	$\Delta G° = -102.$ kJ/mol	thermodynamically favored (rule of -25)

Combining equations requires the **addition of Gibbs free** energies of the coupled reaction gives the net reaction $\Delta G°$.

Combining (adding) equations requires multiplying the equilibrium constants.

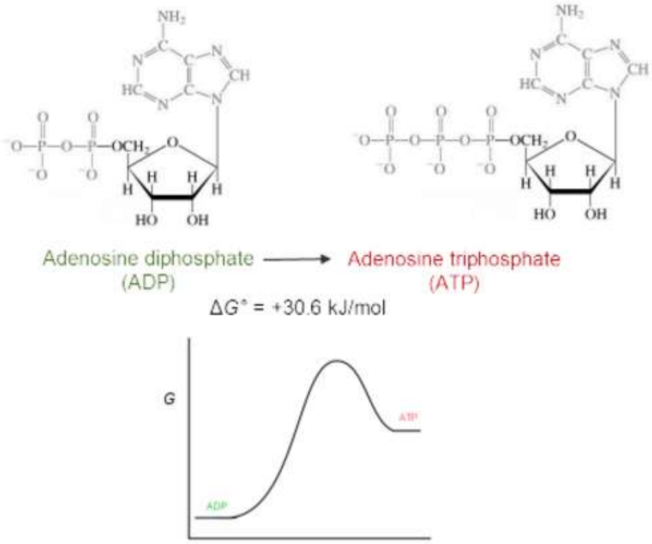
Rxn 1: $ZnS \rightarrow Zn + S$	$K_1 = 2\times10^{-35}$	not any way thermodynamically favored
Rxn 2: $S + O_2 \rightarrow SO_2$	$K_2 = 3\times10^{52}$	totally thermodynamically favored
Net Rxn: $ZnS + O_2 \rightarrow Zn + SO_2$	$K_{net} = K_1 \times K_2 = 7\times10^{17}$	coupled, thermodynamically favored

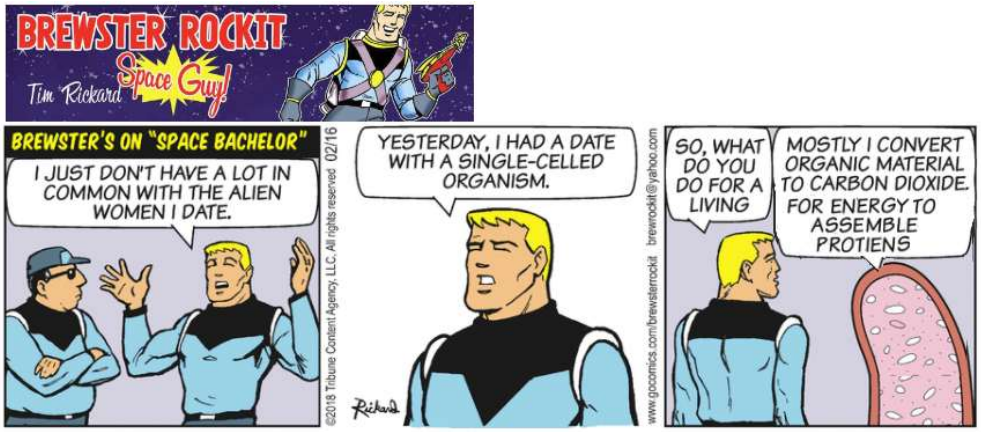
Note: Adding equations multiplies the equilibrium constants!

18.7 Thermodynamics of Living Systems

The one example used in the curriculum guide is the coupled ATP-ADP reaction.

> The coupling of biochemical reactions can justify the production of lower entropy complex substances.
>
> e.g., The ATP-ADP reaction is a thermodynamically favored reaction that has enough negative ΔG to help along the positive ΔG of protein synthesis[3]. This is done through common intermediates (coupling).
>
> ADP can be converted into ATP by cells by oxidizing glucose. The oxidation of glucose's thermodynamically favored reaction is use to Increase the ATP's potential Gibbs free energy.
>
> The higher energy ATP can then be utilized to push along a non-thermodynamically favored process such as building proteins in a coupled reaction.





Brewster is wrong is in saying he doesn't have a lot in common with single-celled organisms since he too assembles proteins through a coupled reaction with the thermodynamically favored ATP-ADP rxn.

> Although not mentioned in this chapter, some thermodynamically "unfavored" reactions can be driven forward with the application of outside energy in the form of electricity. This will be explained in detail in the next chapter.

---

[3] Biology is not my forte, and there may be more accurate explanations for protein synthesis, but my explanation will be good enough in the unlikely case that it is on the AP Chem exam.

The AP Chemistry curriculum emphasizes Kinetic control vs. Thermodynamic control

Kinetic control (rate of a reaction) is determined by the activation energy barrier with the rate constant, k. Kinetic control is how fast the reaction will progress to get to equilibrium.

Thermodynamic control is ΔG and the equilibrium constant, K_{eq}.

Thermodynamic control determines how much product and reactant are present when equilibrium is reached.

This example shows the interplay of kinetic and thermodynamic control.

Running the reaction at lower temperatures may result in a very slow reaction rate, taking a long time to produce the product. By increasing the temperature, equilibrium is reached sooner.

Synthesis of ammonia involves

$\Delta H°$ = exothermic negative $\Delta S°$ = decrease in entropy, negative

$$N_2(g) + H_2(g) \rightleftarrows NH_3(g) + \text{Heat}$$

At a high temperature, 300 °C, the equilibrium shift is left toward the reactants, , . The ammonia reaction has a positive $\Delta G°$ producing a low yield of 27%, but it only takes a few hours to get that 27% yield.

At the lower temperature of 100 °C, the equilibrium shift is toward the products, . The ammonia reaction has a negative $\Delta G°$ producing a higher yield of 92%, but you have to wait years to get that higher yield.

So, for industries that make ammonia, the reaction is run at unfavorable thermodynamic conditions, high temperatures, but the high temperatures allow a faster reaction rate to produce more ammonia within a given time span.